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Insights into the nature of the coupling interactions between uracil corrosion inhibitors and copper: A DFT and molecular dynamics study

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ABSTRACT

In this study, the nature of the coupling interactions between copper and uracil as well as its several derivatives has been systematically investigated employing the atoms in molecules (AIM) theory and energy decomposition analyses. The whole interaction process has been investigated through the analyses of the radial distribution functions of the Cu···X (X = S and O) contact on the basis of the *ab initio* molecular dynamics. No direct relationship between the adsorption strengths and inhibition efficiencies of the inhibitors has been observed. Additionally, the possibility of the methyl-substituted dithiouracil species to act as copper corrosion inhibitors has been tested.

1. Introduction

As one of the most commonly used metals, copper (Cu) has a wide range of applications in the chemical and electronic industry due to its good properties [1]. Generally, Cu is resistant toward the influence of atmosphere and many chemicals. However, it is known that it is susceptible to corrosion in aggressive media. To retard or stop the corrosion process, the use of copper corrosion inhibitors is necessary as a convenient and economic method. These corrosion inhibitors molecules can be adhered to the metal surface and form a film that retards metal dissolution [2]. Until now, lots of inorganic and organic substances especially for heterocyclic compounds containing one or more S, N, and P atoms have been used in the corrosion process of Cu. Here, the most commonly used copper corrosion inhibitor is benzotriazole, which is applied widely in various media for the corrosion inhibition of Cu [3–8].

Owe to the specific structural aspects and properties, uracil and its derivatives can also be used as efficient corrosion inhibitors besides their applications in biological and pharmaceutical fields as mutagenic, anticancerogenic, and antithyroidien character [9]. In particular, uracil (**Ur**) and its substituted derivatives including 5,6-dihydrouracil (**DHUr**), 5-amino-uracil (**AUr**), 2-thiouracil (**TUr**), 5-methyl-thio-uracil (**MTUr**), and dithiouracil (**DTUr**) have been tested as corrosion inhibitors of copper experimentally [9]. The inhibition efficiency decreases in the following order: **DTUr** > **MTUr** > **TUr** > **Ur** > **DHUr** > **AUr**, where the **DTUr** has been confirmed to be the best inhibitor among them. Theoretically, the inhibitive effect of the selected substituted uracils, such as **DTUr**, **TUr**, **Ur**, and **DHUr**, against the corrosion of neutral copper surface is studied by means of the density functional approach B3LYP/6-31G calculations [10]. It was found that the dipole moment and the separation energy ($\Delta E_{HOMO-LUMO}$) between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are directly correlated with the inhibition efficiency of the inhibitors. Namely, the inhibition efficiency increases with the increasing of the dipole moment and the decreasing of the separation energy.

Despite the extensive studies on the corrosion inhibition of Cu by the uracils mentioned above, the relevant details, such as the thermodynamic parameters, adsorption strengths, and the evolution of the adsorption modes in the corrosion inhibition process, still remain unclear to the best of our knowledge. Obviously, the clarification of these problems is crucial for the better understanding of the corrosion inhibition mechanism and the control of the corrosion processes. In the absence of the experimental information, a theoretical investigation of these problems is highly desirable since quantum chemical calculations have been proven to be a powerful tool to study the fundamental and molecular-level processes related to corrosion inhibition [11–28].

Therefore, in the present study, the coupling interactions between the above uracil derivatives and copper have been detailedly investigated employing the density functional theory (DFT) in combination with the atoms in molecules (AIM) theory, the energy decomposition analysis (EDA), and *ab initio* molecular dynamics. It was found that the favorable coupling modes between Cu and high efficient corrosion inhibitors have been verified by the *ab initio* molecular dynamics. The coupling interactions between Cu and uracils are predominated by both the electrostatic and orbital interactions. Moreover, there is no direct relationship between

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the adsorption strengths and the inhibition efficiency of the inhibitors. The electron transfer behavior upon the formations of the Cu–inhibitor complexes are different for the high and low efficient inhibitors through the natural charge analyses. Additionally, the possibility of the four methyl-substituted dithiouracil species to act as copper corrosion inhibitor has been proposed. Hopefully, the present study can provide some helpful clues to the microscopic corrosion inhibition mechanism and the molecular design of novel Cu corrosion inhibitors based on the uracils.

2. Computational methods

In the present study, the popular Becke's three-parameter hybrid functional (B3LYP) method [29,30] in combination with the 6-311++G(d,p) basis set has been chosen, where the reliability and efficiency of the method has been verified by the previous investigations on the relevant systems [31–34]. Namely, all the geometries have been fully optimized at the B3LYP/6-311++G(d,p) level of theory. Subsequently, vibrational frequency analysis has also been performed at the same level of theory in order to identify whether the optimized structures correspond to a true local minimum or not.

To better clarify the nature of the intermolecular Cu···X (X = S and O) contact in the formed Cu–inhibitor complexes, the atoms in molecules (AIM) theory has been employed on the basis of the optimized structures. In the AIM analyses [35], the existence of the interatomic interaction is indicated by the presence of a so-called bond critical point (BCP). The strength of the bond can be estimated from the magnitude of the electron density (ρ_{bcp}) at the BCP. Similarly, the ring or cage structures are characterized by the existence of a ring critical point (RCP) or cage critical point (CCP). Furthermore, the nature of the interatomic interaction can be predicted from the topological parameters at the BCP, such as the Laplacian of electron density ($\nabla^2\rho_{bcp}$) and energy density (H_{bcp}). Generally, the sign of $\nabla^2\rho_{bcp}$ reveals whether charge is concentrated ($\nabla^2\rho_{bcp} < 0$) as in covalent bonds (shared interaction) or depleted ($\nabla^2\rho_{bcp} > 0$) as in ionic bonds, H-bonds, and van der Waals interactions (closed-shell interaction). It is also reported that if $\nabla^2\rho_{bcp} > 0$ and $H_{bcp} < 0$, then the interaction is only partly covalent in nature [36–39]. Additionally, to further evaluate the electron transfer behavior between Cu and inhibitors, natural bond orbital (NBO) analyses [40] have also been carried out employing the more flexible 6-311++G(3df,3pd) basis set.

To characterize the adsorption strengths for uracils on the Cu surface, the binding energy ΔE has been introduced, which is defined as the energy difference between the formed Cu–inhibitor complex and the corresponding monomers. Moreover, zero-point vibrational energy (ZPVE) corrections and basis set superposition errors (BSSEs) calculations have also been considered, where the Boys–Bernardi counterpoise technique has been employed to evaluate the BSSEs [41]. All the calculations mentioned above have been performed using Gaussian 03 program [42].

Furthermore, to gain a more detailed insight into the nature of the coupling interactions between uracils and Cu surface, the energy decomposition analysis (EDA) is carried out based on the methods of Morokuma [43] and Ziegler and Rauk [44]. Generally, the total binding energy can be divided into two major components as follows:

$$\Delta E = \Delta E_{prep} + \Delta E_{int}$$

where the preparation energy ΔE_{prep} is the energy that is necessary to promote the fragments (corrosion inhibitors) from their equilibrium geometry and electronic ground state to the geometry and electronic state which they have in the complexes. ΔE_{int} is the instantaneous interaction energy between two fragments in the complex, which is the focus of the binding analysis below. Moreover, the ΔE_{int} can be further divided into three physically meaningful components:

$$\Delta E_{int} = \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{orb}$$

where ΔE_{elstat} is the electrostatic interaction between the fragments and is calculated with a frozen electron density distribution in the geometry of the complex. ΔE_{Pauli} is the repulsive interaction between the fragments that are caused by the fact that two electrons with the same spin cannot occupy the same region in space. The last term ΔE_{orb} is the orbital interaction, which accounts for the stabilizing orbital interactions between occupied and virtual orbitals of the two fragments. Usually, both the ΔE_{elstat} and ΔE_{orb} terms are negative and play a positive role in stabilizing the whole complexes. The energy decomposition analyses have been performed at the BP86/TZ2P level of theory employing the ADF program [45] on the basis of the optimized geometries at the B3LYP/6-311++G(d,p) level of theory.

To further verify the reliability of the above results associated with the adsorption modes and adsorption strengths, periodic density functional calculations using the DMol^3 program [46] have been carried out for three representative corrosion inhibitors **DTUr**, **Ur**, and **AUr** on the Cu(1 1 0), Cu(1 0 0), and Cu(1 1 1) surfaces. The generalized gradient-corrected (GGA) functional developed by Perdew and Wang (PW91) [47,48] has been employed in conjunction with a double numeric quality basis set with polarization functions (DNP), where the reliability of this level of theory in studying the Cu surface has been confirmed [49]. The electron–ion interaction was described by density functional semicore pseudopotentials (DSPPs) for metals, which are intended for use with density functional local orbital methods. A Fermi smearing of 0.005 Hartree and a real space cutoff of 4.4 Å were used to improve computational performance. The convergence criteria on the energy, gradient, and displacement were set to 1×10^{-5} hartree, 2×10^{-3} hartree Å^{-1}, and 5×10^{-3} Å, respectively.

As for the simulations of Cu surface, periodic slab models have been employed. In more details, the calculated lattice constant of 3.66 Å, which is 1.4% larger than the experimental value of 3.61 Å [50], was used to build a four layer slab and (4×4) supercell of Cu surface. All these slabs are separated by a 16 Å vacuum thickness to ensure that the interaction between the periodically repeated slabs along the normal of the surface is small enough. A $3 \times 3 \times 1$ k-point sampling was used for all the slabs. During the geometry optimizations, two top layers of the slab model and the corrosion inhibitors were allowed to relax, while two bottom layers of the slab were frozen in the bulk positions. The binding energy of the adsorption is calculated by subtracting the energies of the corrosion inhibitors and the Cu surface from the energy of the adsorption system.

Additionally, to further confirm the adsorption modes adopted in the corrosion inhibition processes dynamically, the *ab initio* molecular dynamical calculations at the BLYP/DNP level of theory have been carried out employing the DMol^3 program on the basis of the optimized geometries at the B3LYP/6-311++G(d,p) level of theory. Constant temperature simulations are achieved by using the Nosé–Hoover chain at 298.15 K and the total simulation time is 3 ps with a time step of 1 fs. Furthermore, the radial distribution functions (RDFs) for the Cu···X (X = S and O) contact distance have been constructed based on the molecular dynamics.

3. Results and discussion

3.1. Interaction modes and AIM analyses

All the most stable Cu–inhibitor complexes have been displayed in Fig. 1, where the nomenclatures of the studied uracils are